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CONTENTS

ON THE FLOW OF AIR THROUGH CHINK OF A REED VIBRATOR

By

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This paper gives a report of the experimental work on the flow of air through chinks in the case of (1) stationary and (2) vibrating reeds. The production of sound waves by the periodic efflux of air through the variable chink of a vibrating reed is a well known phenomenon and has applications as acoustical sources. The present experimental work was undertaken to determine the nature of air flow as it comes out of the chink and the resulting pressure changes in the outer regions of the flow. We have found a zone of negative pressure on the rear side of the reed showing that Kirchoff's law of flow are not obeyed. Similar zones have been observed earlier by Fage and Johansen (1927) in the case of flow behind an inclined flat plate.

We have also studied for the first time the variation of pressure with time near the chink. By taking into account the effect of viscosity on air flow and by a modification of the theory of Ghosh (1946) on maintained vibration, we have been able to account for the phenomena in a general way. There is a good similarity between the experimental and theoretical curves which suggests that viscosity does play an important part in the flow of air.

The experimental work was divided into two parts. In the first part measurements of velocity of flow were taken and in the second pressures at different points were measured. These observations were

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taken for both stationary and vibrating reeds. Study of variation of pressure with time has been done by oscillographic method.

To achieve these the outlet end of a wind tunnel was closed with a wooden disc to which was screwed a small wooden box. There was a rectangular slit in the wooden disc to allow wind to enter the box and in order to minimise the streaming motion from the wind tunnel, waste cotton padding was inserted in the proper places. This was done to simulate the condition of the case of harmonium reed vibrator where static pressure is developed with the help of bellows. By this device sufficient pressure was developed within the box. The magnitude of the pressure developed in the box was adjusted by the speed of the blower.

The reed vibrator was housed in a slot $1'' \times 4\frac{1}{2}''$ made in a brass plate $1/8''$ thick which was screwed to the lid of the box. The reed was arranged to be in flush with that surface of the brass plate which faced the interior of the box and thus chink was formed when the reed moved towards its inward position. In the case of stationary reed observations it was kept slightly inclined to the plane of the slot so that air would issue out through the chink which was formed along the length and the tip of the reed. Observations were taken over the reed at different points in one plane. The observations were repeated for planes at different heights.

VELOCITY MEASUREMENTS

For measurements of velocities a hot wire anemometer was used. As the direction of air greatly influences the cooling effect, the anemometer wire was placed in such a manner that the wire was always normal to the wind flow in which position the cooling effect is maximum. This was assured by placing the wire parallel to the longer edge of the reed. Length of the anemometer wire was chosen to be suitably small in order that it may record air flow at a point which may be taken to be the middle point of the wire. Further the leads to the wire were oriented practically parallel to the direction of wind flow in order that they may produce least disturbance at the point of observation. The current through the anemometer wire was adjusted with the help of a series variable resistance such that in the absence of

any air flow, the anemometer wire became red hot. The current was noted. The potential difference E_0 across it, for the wind velocity zero, was measured by a potentiometer. For measuring velocity of air flow 'v' at a point, the anemometer wire was placed in confirmity of above requirements the current through it was adjusted to the above noted value and the potential difference across the wire E_v was recorded. In order to minimise any change in current due to change in the resistance in the hot wire, the variable resistance used in series with it was chosen to be suitably large. The instrument was found suitable for measurements of small wind velocities of our experiments. For practical purposes we may take the wind velocity to be given by $v = k\sqrt{E_0 - E_v}$ where k is a constant of proportionality. In the case of vibrating reed as the velocity of air is not constant, $k\sqrt{E_0 - E_v}$ gives the r. m. s. value of the velocity. Measurements of velocity were taken at different points in a plane of line of flow lying at fixed height above the reed, the least height in the case of vibrating reed being arranged so that the reed did not touch the hot wire.

For measurements of average dynamic pressure, a special inclined manometer was constructed. It was made out of a glass tubing about 4 mm. in diameter, the extended part of the manometer being formed into a glass probe, the end of which was closed and a small hole of the size of 2 mm. diameter was made very near to it. The tube was placed in such a manner that the flow of wind was tangential to the surface of the hole at the point where measurement of pressure was desired to be taken. The manometer orifice was purposely made small and the edges of the hole were smoothened so that no sharp ridge was projected against the flow of air, as any ridge would slacken the velocity with consequent development of stagnant pressure near the orifice. In taking pressure readings which are small, parallax error was avoided by placing a second scale about 5 ft. behind the manometer scale.

In the case of vibrating reed, the absolute values of r.m.s. pressures at various points were found out with the help of a calibrated Western Electric 640 AA type microphone and associated amplifier. A small brass probe was used for measurement of pressure at a point; the attenuation due to probe was neglected as the frequency of pressure variation

was small. Figure 4 shows the r.m.s. pressure curve. We find the r.m.s. value comes out to be about 70% of the constant pressure inside the chamber. This is the order of the r.m.s. value predicted from our theoretical consideration (see figure 7) given later.

Observations :—

Plane of observation :—Normal to the plane of the slot in the brass plate and one centimeter from its shorter free end.

x and z are two perpendicular directions in the plane of observation with the edge of the slot as origin, values of x being measured towards the middle of the reed in a direction parallel to shorter free end of the slot.

(A) *Velocity Observations :* —

Constant current through anemometer wire $= 0.7$ amps.

E. M. F. across hot wire (E_o) for zero velocity of air $= 1.7225$ volts.

Vibrating reed.

Distance across the reed 'x' cm.	Height $z=3$ mm.		Height $z=5$ mm.		Height $z=1$ cm.		Height $z=2$ cm.	
	E_v	$\sqrt{(E_o-E_v)}$	E_v	$\sqrt{(E_o-E_v)}$	E_v	$\sqrt{(E_o-E_v)}$	E_v	$\sqrt{(E_o-E_v)}$
—·4	1·3716	·593	1·3918	·575	1·4036	·565	1·4824	·490
—·2	1·2960	·653	—	—	1·3364	·622	1·4250	·546
0	1·2460	·690	1·2588	·681	1·3041	·647	1·3705	·593
·2	1·1673	·745	1·2194	·709	1·2580	·681	1·3150	·638
·4	1·1275	·771	1·1717	·742	1·2208	·703	1·2675	·675
·6	1·1120	·782	1·3750	·765	1·1890	·730	1·2707	·707
·8	1·1365	·765	1·1254	·772	1·1607	·749	1·1870	·731
1·0	1·1820	·736	1·1394	·763	1·1540	·754	1·1673	·745
1·2	1·2460	·690	1·1878	·731	1·1670	·745	1·1690	·743
1·4	1·2345	·699	1·1943	·727	1·1730	·740	1·1678	·744

These curves show that the velocity with distance relations have remarkable similarity in the cases of vibrating and stationary reeds.
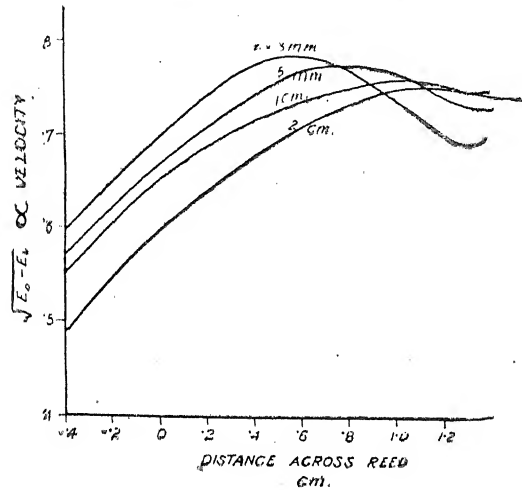

Fig. 1

So we may conclude that the stream lines of flow are similar in the two cases. Further from the graphs we find that the maxima of velocity curves approaches the centre of the reed asymptotically as we go higher above the plane of the reed.
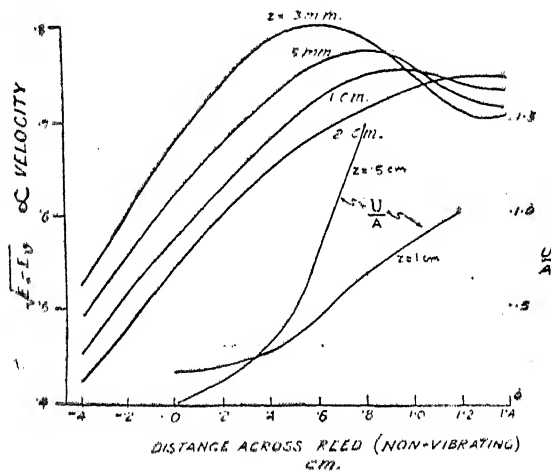

Fig. 2

(*B*) *Pressure Observations :—*

The following tables show the pressure observations which were taken with the help of apparatus described earlier.

Stationary Reed

Distance across the reed 'x' cm.	Heights 'z' in cm. for the undernoted pressures in mm. of alcohol									
	−1·25	−1·00	−·75	−·50	−·25	0	·5	1	2	3
0					·3	3 to ·5				
·2					·2 to 0	3 to ·35				
·4				35	·55, ·10	3 to ·7				
·6			·75 to ·45	·9, ·3	1 05, ·2	3 to 1·3 & −.25				
·8	·9 to ·7	1·0, ·55	1·2, 45 53	1·3,	1·3, ·25	3 to 1·8 & 0	−1	−·2		
1·0	1·15 to ·75	1·35 to 6	1·5, ·5	1·65, ·4	1·85, ·3	3 to 1·8 & .2	·1	0		
1·2		1 0	1·35, ·6	1·8, ·45	2·0, ·35	3 to 2·6 & .3	1·5	·05	−·10	−·35

Vibrating Reed—r. m. s. Pressure

Pressure p inside chamber	Height z in cm.	r. m. s. Pressure in Dynes/Sq. cm.								
		$x=.4$ cm.	$x=-.2$ cm.	$x=0$ cm.	$x=.2$ cm.	$x=.4$ cm.	$x=.6$ cm.	$x=.8$ cm.	$x=1.0$ cm.	$x=1.2$ cm.
380 dynes	·5 cm.	70	100	135	182	231	252	254	235	219
per	1	65	80	110	158	215	236	245	238	235
Sq. cm.	2	50	62	75	93	133	220	240	215	195

Amplitude ξ_0 of vibration of reed = 0·7 cm.

The isobars in the cases of stationary and vibrating reeds are similar. We make the following observations from the curves. The curve for normal pressure starts from a height of about 5 mm. from

DISTANCE ACROSS PLATE IN CM.
FIG. NO. 3
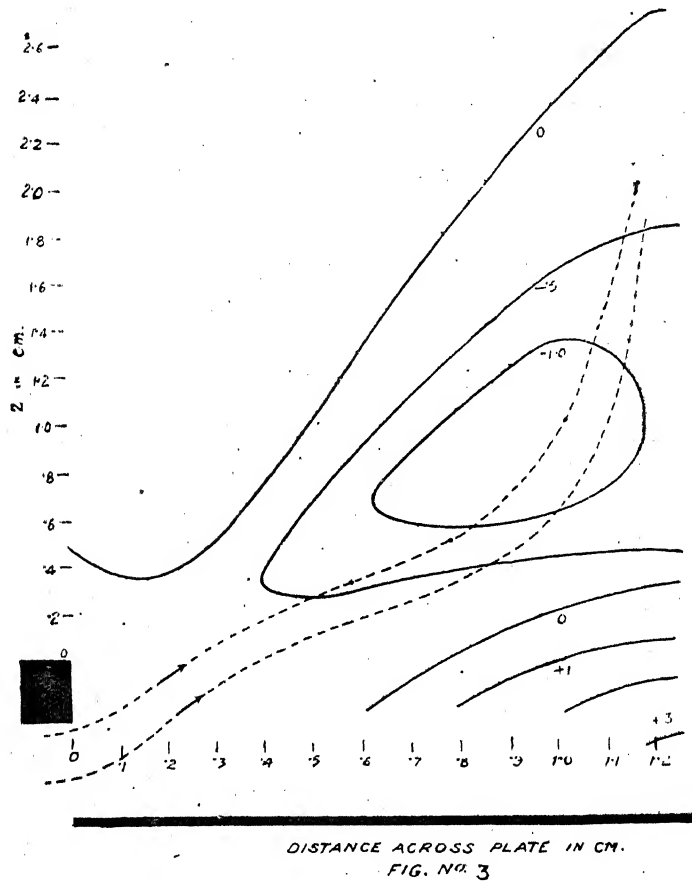
the upper plane of aperture. It rises very quickly towards the middle of the reed and reaches a height of about 2·7 cm. at the middle of the reed. Lower down of this isobar is the isobar of − ·5 mm. which does not continue upto chink but bends round at a distance of 4 mm. across the reed. Practically enclosed by this isobar is the isobar of − 1·0 mm. which indicates that the zone of maximum negative pressure is at a height of one cm. and at a distance of ·8 cm. across the reed. As we go lower down from this zone of maximum negative pressure, we meet isobars with increasing pressure till finally just at

the back of the middle portion of the reed the pressure is about 3 mm. The zone of negative pressure on the reed has been marked, which
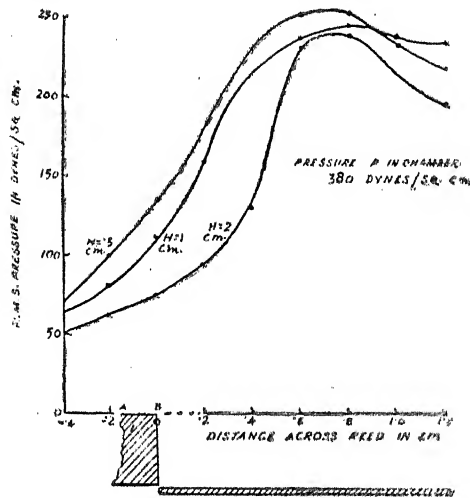

Fig. 4

ought not to have been there according to Kirchoff's law. Observations of the pressure very near the mean position of reed in the vibrating case could not be taken due to vibratory motion of the reed, but as we have established that stream lines of flow are similar in the two cases, we conclude from the observations on the stationary reed, that there exists a zone of negative pressure just at the back of the reed near chinks and that the mid region between the chinks is a zone of excess pressure.

From the nature of isobars, as also from the considerations of points of maximum velocity at given heights we can draw the stream lines as indicated by the dotted lines in the graph for stationary reeds.

Phase Relation Between Chink Width And Pressure

It is very important to know in what manner the chink width changes and the pressure in the outside regions follows the changes or lags behind. In order to investigate these questions the pressure changes near the reed were photographed by means of an oscillograph.

In order to determine the phases of maximum and minimum pressure changes with the variations of the chink width due to upward and downward motion of the reed the following device was made.

A bent tube, with orifice as in the case of the probe of manometer, lead the pressure variations into a brass chamber specially designed to enclose a carbon microphone. The resulting electrical impulses due to pressure variations were applied through a transformer to the vertical deflecting plates of an oscillograph after amplification, a synchronised sweep frequency being applied to the horizontal deflecting plates. In order to mark the phase of vibration of reed in the resulting pressure-variation pattern a bent wire was fixed in such a manner that the reed in one of its two extreme positions of vibrations just touched the wire and there by short-circuited the secondary of transformer. As the microphone voltage applied to oscillograph got short circuited, dots appeared on the pattern at such instances. We should make an allowance of 90° in phase as the secondary voltage is so much out of phase with primary current which is in phase with pressure variation. A photograph for pressure variations at a point 1·5 cm. from the chink and in the plane one centimeter from the
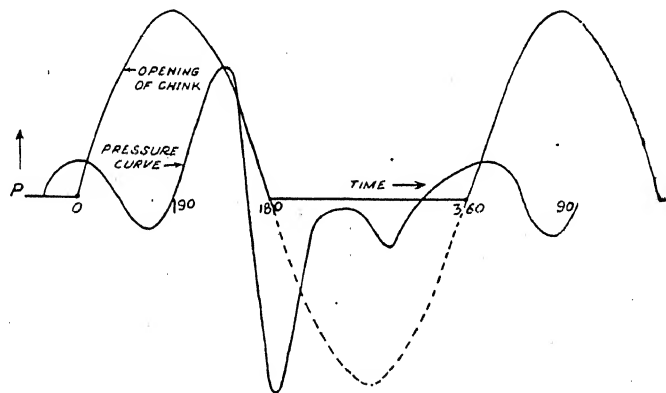
Pressure Variations near Chink.

Fig. 5

shortest edge of the seat for reed was taken and a figure showing the associated chink width variations was drawn out of it.

In the case of the figure showing the pressure variations just near the chinks we observe that just as the reed begins to move downwards

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i.e., just as the chink begins to open pressure is slightly positive, as the chinks open further the pressure becomes slightly negative. It is slightly positive when the chink is open to its maximum extent. After this instant the reed retraces back towards its mean position and the pressure increases and becomes large. Just before the chink is closed the pressure decreases rapidly and becomes zero. When the reed reaches its mean position the pressure becomes maximum negative. Now as the reed moves upward, the chink is practically closed and negative pressure predominates for a major part of this half cycle. It was observed from the figures* that the average pressure very near the back of the reed is negative in the regions near the chinks and is positive midway between the chinks. The same conclusion was arrived at by manometric observations.

### Pressure and Chink-width Relation

From the nature of the flow pattern and isobars it is apparent that the flow behind the chink is governed largely by viscosity of air and laws of potential flow are departed from. We assume that the flow velocity u is given by

$$u = K . \triangle P \xi$$

where, K is conductivity of the chink (dimension LT/M). This will hold true as long as the chink is fine and viscosity is the predominant factor in determining the flow. Hence the volume of air flowing through the chink per second will be given by

$$Q = K . \triangle P . \xi^2 b \qquad\qquad (1)$$

where b represents the effective length of the chink. $\triangle P$ is the difference of pressure between the zones A and B as shown in the figure. Though in our case the flow is not exactly similar as will be clear from the following diagram but the flow will be dimensionally similar and Q will be given by an expression similar to (1) excepting that the constant K will be different in the two cases.

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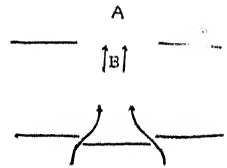
*Other figures not given in the text.

In the present case since the wave-length is large the air issuing out of the chink will behave like an incompressible fluid in the neighbourhood of the chink and then we can take the above equation to hold true in this case.

In the case of a vibrating reed the chink width will simply be the displacement of the reed from its normal position. Using the formula (Ghosh 1946) for excess pressure 'p' in the outside regions we get.

$$p = \frac{c\rho}{2\pi R^2} \cdot \frac{j\omega Q}{(c/R + j\omega)} \qquad (2)$$

Since $\Delta P = P - p$, by combining equations (1) and (2) we get.

$$p = PKb \cdot \frac{\xi^2}{Kb\xi^2 - j\dfrac{2\pi R}{\omega\rho} + \dfrac{2\pi R^2}{\rho c}} \qquad (3)$$

Where P represents the constant excess of pressure within the chamber. ξ will be given by

$$\xi = \xi_0 e^{j\omega t} \qquad (4)$$

The real part of which represents the displacement of the reed, viz.

$$\xi = \xi_0 \cos \omega t \qquad (5)$$

Substituting the exponential value of ξ in equation (3) we get.

$$p = P \frac{\xi^2_0 (\cos 2\omega t + j \sin 2\omega t)}{\xi^2_0 (\cos 2\omega t + j \sin 2\omega t) - j\dfrac{1}{Kb} \cdot \dfrac{R}{f\rho} + \dfrac{2\pi}{c\rho} \cdot R^2 \cdot \dfrac{1}{Kb}} \qquad (6)$$

In our case, $R = 1.5$ cm., $f = 46$ cycles/sec, $b = 5.8$ cm., $\xi = 0.7$ cm.

Taking the following values for the constants, $K = 5$ cm. sec, gm^{-1}., $\rho = 1.25 \times 10^{-3}$ gm/c.c., $\rho c = 42$,

The amplitude of 'p' for various values of 'pt' has been calculated from the equation (6) and the curve plotted as in below. By comparing this diagram with that obtained by oscillographic record we observe that the two curves are similar except for a change of phase. We expect some change of phase to occur because of some finite inductance in the primary of the transformer used in the microphone

circuit. We find the negative amplitude of pressure to be larger in both the cases. The similarity between the experimental curve
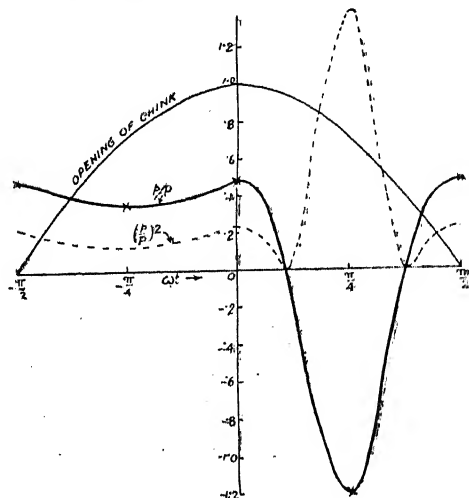

Fig. 7

and the curve predicted by the law of slow motion under viscosity shows that viscosity plays an important part in the flow of air through chink of a reed vibrator. The vibrating reed practically closes down the chink for one half of its period of vibration and consequently this part of flow has not been dealt with.

Fig. 6, shows also the plot of the square of theoretical pressure for the interval the reed opens. From this by measurement of area in Fig. 7, we find that the r.m.s. value of pressure at the point under consideration is about 70% of the pressure P inside the chamber as was observed experimentally.

Velocity Curves

At large distances from the aperture it has been found (Roscoe 1949) that the radial velocity U at a distance r is given by

$$U = \frac{2Az^2}{r^4} \tag{7}$$

where z is the perpendicular distance from the plane of aperture. The two curves plotted in the velocity diagram (Fig. 2) are those calculated out from equation (7). Although the condition required by the equation are not fully realised but there is similarity between the two

curves. It has been possible to make quantitative measurements and thus to verify the theory developed.

Conclusion

The paper gives an account of measurement of 'flow' through chinks of (1) constant width and (2) the same in the case of chink of periodically varying width. The types of flow in both cases have been found to be similar. The flow is least near the chink and increases as the point of observation is moved along one plane towards the dead centre; definitely there is a region of maximum flow before reaching the dead region. If the plane of observation is raised higher the same type follows but the maximum shifts towards left (Fig 1 and 2). The pressure measurement were done with a manometric probe; the isobars are shown in figure (3) in the case of a chink of fixed width. The measurements in the case of a chink of variable width gave a mean value which was not found to be accurate but the type of isobars was practically similar.

It has been found that the flow is governed by viscosity and the law formulated by Roscoe seems to hold true in the case of chink described in the text. The volume rate of flow is proportional to difference of pressure and to the square of the chink width in the case where the length is large in comparision to the width. A comparision of the pressure time curve with the oscillographic record shows remarkable similarity in the case of a chink of periodically varying width. The theory developed has been quantitatively verified experimentally.

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A QUALITATIVE STUDY OF FLAME TEST FOR TIN, GOLD AND BISMUTH

By

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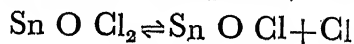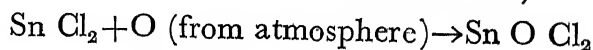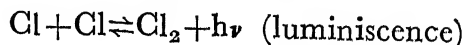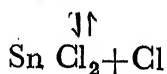
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A blue mantle test for tin has been described by H. Meissner[1] as follows: 'The substance or solution is treated in a porcelain dish with an excess of hydrochloric acid and a piece of pure zinc rod is added. The mixture is well stirred by means of a test tube filled with cold water and the tube is then inserted into a non-luminous flame. A blue mantle around the moistened part of the tube indicates the presence of tin.' F. L. Hahn[2] tried to find out the cause of the above test and came to the conclusion that probably the blue luminiscence is not due to the formation of stannic hydride as was assumed by Meissner. E. Schroer and A. Balandin[3] find that the blue luminiscence cannot be due to the excitation by free electrons. J. Hoffmann[4] applied the test to glass analysis and again describes the test to appear by the reduction of glass by zinc and hydrochloric acid which affords SnH_4 and this SnH_4 deposits on the cold surface of the tube and colours the flame blue.

The test in all probability is not due to the formation of tin hydrides. It was observed by Salet[5] and later confirmed by Bancroft and Weiser[6] that the tin chlorides themselves colour the Bunsen flame blue, the tin bromides colour it green and the iodide imparts a yellow colour to the flame. Therefore, the test for tin was repeated in the manner described by Meissner and it was found that if stannous or stannic chloride itself is dissolved in water and a test tube full of water placed in the solution, then when the test tube is brought to

the Bunsen burner, a blue mantle surrounds the bottom of the test tube. The only perceptible effect of addition of zinc and hydrochloric acid is to increase the intensity of the blue luminiscence. If the tin chloride is replaced by tin bromide or iodide, the colour of the mantle was respectively green and yellow. However, when the test is repeated with zinc and sulphuric acid in the place of hydrochloric acid, no blue mantle appears at all. It was found that the presence of sulphate, nitrate or fluoride ions inhibits the test, when their alkali salts are added in sufficient quantity to a mixture of tin salt, zinc and hydrochloric acid. The appearance of the blue mantle with tin salts alone makes the hydride theory very improbable. It might be argued that the free hydrogen present in the gas supplied to the Bunsen burner might be playing a part, but the instability of the tin hydride as prepared by Paneth and Furth[7] by the action of metallic magnesium on a solution of tin chloride or sulphate in hydrochloric acid rules out the above line of argument. Moreover, the non-appearance of the test when hydrochloric acid is replaced by sulphuric acid cannot be explained by the hydride theory. As was shown by Schroer and Balandin[8] who suggested that the method may be used for halogen acid, the reaction is a test of the chloride, bromide and iodide ions rather than that of tin. The chloride and bromide ions, somehow exhibit the test in the presence of tin ions. It occurred to the author that it may be a case of chemiluminiscence brought about by the recombination of halogen atoms formed from the dissociation of the tin salt according to the following scheme :

$$SnCl_4 \rightleftharpoons SnCl_3 + Cl$$
$$\Updownarrow$$
$$SnCl_2 + Cl$$

$$Cl + Cl \rightleftharpoons Cl_2 + h\nu \text{ (luminiscence)}$$
$$SnCl_2 + O \text{ (from atmosphere)} \rightarrow SnOCl_2$$
$$SnOCl_2 \rightleftharpoons SnOCl + Cl$$
$$\Updownarrow$$
$$SnO + Cl$$

Similarly, $Br + Br \rightarrow Br_2 + h\nu$ (luminiscence)
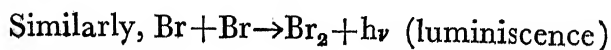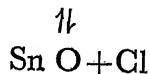
The order of the luminiscence observed may be taken from the convergence limit of chlorine and bromine in their predissociation spectra. The convergence limits of chlorine and bromine are at 4785° and 5107° A, which lie in the blue and green region respectively. The heats of dissociation of chlorine and bromine are 57000 and 46200 calories respectively and so the wave-length of the light emitted on the recombination of the atoms would be 4987° and 6147° A respectively (from $Q=h\nu=hc/\lambda$).

If the above mechanism about the test were correct, similar colours must be observed from the chlorides and bromides of all metals where tendency to similar thermal dissociation exists. On applying this test, it was found that mercuric, thallium, platinum, manganese, cobalt, lead, nickel, cadmium and arsenic salts do not show any similar coloration. However, it was found that bismuth and gold salts do show similar tests. The purpose of the present communication is primarily to describe the flame test for gold which is of practical importance, and to describe the similar coloration of the luminiscence that is shown by bismuth and gold salts so that it may not be confused for the blue luminiscence shown by tin salts in the Meissner's test. It further describes the interfering factors in the presence of which the flame test for tin is suppressed.

Flame reactions of tin salts :

Stannic and stannous chloride gave a very brilliant blue mantle, which increased in intensity on the addition of hydrochloric acid. Action of zinc further does not appear to have much influence. The blue luminiscence is suppressed if the hydrochloric acid is replaced by sulphuric acid and the test does not appear even when zinc is added in the presence of sulphuric acid. The blue luminiscence is also suppressed by the addition of ammonium sulphate, nitrate or fluoride to the tin salt. In the presence of hydrochloric acid, larger quantity of sulphate, nitrate or fluoride ions is necessary to suppress the test than without it.

Stannic bromide gave a brilliant green mantle which increased in its intensity with the addition of hydrobromic acid. If hydrochloric acid is added in the place of hydrobromic acid, the green mantle characteristic of the bromide is replaced by the blue mantle characteristic of the chloride. If the amount of hydrochloric acid is small or the solution to be tested contains some other source of the bromide ions, so that the amount of bromide ions present is comparable with the amount of the hydrochloric acid added, then the green luminiscence also appears when the blue luminiscence has faded away.

Stannic iodide gave a greenish yellow mantle and showed a behaviour similar to that of the bromide with hydrochloric acid.

Tin sulphate and nitrate did not show any blue luminiscence either when alone or in the presence of sulphuric acid and zinc. The luminiscence appeared on the addition of concentrated hydrochloric acid, but was again suppressed when sulphate or nitrate ions are added in considerable amounts.

Flame reactions of bismuth salts :

As the chloride, bromide and iodide of bismuth were not obtainable in pure form, a pure Kahlbaum sample of Bismuth carbonate (tested to be free from tin) was taken and the flame test applied in a manner similar to the Meissner test for tin .

Bismuth carbonate with hydrochloric acid gives a greenish blue mantle. Addition of zinc begins to precipitate metallic bismuth and does not improve the intensity of the mantle. However, the test remains positive so long as all the bismuth ions have not been removed from the solution. Addition of tin salt, however, replaces the greenish blue mantle of bismuth chloride by the intense blue luminiscence characteristic of tin chloride.

Bismuth carbonate and hydrobromic acid gives a yellowish green mantle.

Bismuth carbonate and hydroiodic acid gives a very insensitive reddish mantle.

Bismuth carbonate with sulphuric acid and nitric acid does not give any perceptible mantle at all. Addition of small amounts of hydrochloric acid also in the presence of either of these acids does not make the mantle appear.

Flame reactions of gold salts:

On applying the flame test to gold chloride in a manner similar to that described by Meissner for tin, a gold chloride solution in the presence of hydrochloric acid gave a brilliant green mantle. The gold chloride solution itself gives the mantle and along with the appearance of the green luminiscence, a film of brightly shining metallic gold is deposited on the bottom of the test tube. The mantle becomes much more intense in the presence of considerable concentrated hydrochloric acid. Addition of a speck of metallic zinc improves it slightly. The test, like the similar test of the bismuth and tin chlorides is suppressed by the presence of a considerable amount of sulphuric or nitric acid.

Gold chloride solution in the presence of hydrobromic acid gives a pale orange mantle which is not improved much in its intensity even on the addition of metallic zinc.

Gold chloride solution in the presence of hydroiodic acid does not give any mantle. This is probably due to the decomposition of the auric iodide with the simultaneous deposition of iodine.

On the basis of the above reactions, a green mantle test for gold has been recently described[9]. To perform the test, the gold salt solution is taken in a beaker, concentrated hydrochloric acid added to it and a small speck of zinc is put in. A test tube full of water is held at the point where hydrogen is evolving out briskly and then the test tube is taken to the hottest part of the Bunsen flame. If gold

is present in the solution being tested, a very brilliant green mantle will surround the bottom of the test tube spreading upwards along the sides of the tube. The test is sensitive to $0\cdot1$ mgm. of gold per ml. of the concentrated hydrochloric acid. The test is not interfered by the presence of mercury, lead, silver and platinum ions and so gold is easily detected in an ore or alloy by dissolving the nitric acid insoluble portion in a little aqua regia, evaporating almost to dryness to drive out the nitic acid and then applying the above test. The presence of tin however interferes, replacing the green mantle by the blue mantle characteristic of tin. Copper ions also interfere

The mechanism of the above flame reactions:

Much more quantitative and spectroscopic work is essential, before any definite conclusions as to the cause of the above tests can be reached. Though the purpose of the present communication is mainly practical, it may be mentioned that the scheme suggested above drives support from the similarity in the colours of the mantles from tin, bismuth and gold chlorides. It is of interest to mention here a similar though an observation unnoticed by workers in this field, of M. Polanyi and G. Schay[10], who studied the chemiluminiscence between the alkali metal vapours and tin halides. They observed that highly diluted flames of alkali metals burning in stannic chloride, bromide and iodide emit intense luminiscent and continuous bands. The bands extend from 400 to $550\mu\mu$ with K and $SnCl_4$, 405 to $540\mu\mu$ with Na and $Sn\ Cl_4$, from 440 to $600\mu\mu$ with Na and $SnBr_4$, and from 500 to $620\mu\mu$ with Na and SnI_4. The intensity of the bands is the greatest in the centre of the band and decreases on either side. It is clear that with the naked eye the luminiscences would appear to be respectively blue, green and yellow in the cases of the chloride, bromide and iodide. The chemiluminiscence is explained by a mechanism shown below :

$$Sn\,X_4 = Sn\,X_3 + X$$
$$2\,Sn\,X_3 = Sn\,X_2 + Sn\,X_4$$
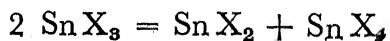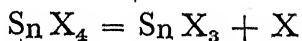
The mechanism is similar to the one suggested above. However, the suggested mechanism also explains the part played by the cool surface of the test tube or hydrogen gas in providing centres of collision for the halogen atoms to unite, for as shown by Jost[11], the recombination of halogen atoms to form the undissosciated molecule can occur only as a three body process in the gaseous phase or on the walls of the nearby solid surfaces.

.However as stated above, much more quantitative work is needed before the mechanism can be definitely established.

Summary

1. The blue mantle test for tin has been studied and it has been found that the colour of the mantle differs with the halide taken. It has been further found that the test is interfered by the presnece of sulphate, nitrate and fluoride ions.

2. Reactions similar to the above have been found to be shown by the halides of bismuth and gold and hence precaution is necessary not to mistake a mantle given by them for the presence of tin.

3. A new sensitive flame test for gold has been described.

4. It has been shown that the blue mantle given by tin cannot be due to the stannic hydride as was supposed. A tentative mechanism has been suggested for the above flame reactions of tin, bismuth and gold.

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THE NATURE OF HYDRATED COPPER HYDROXIDE PRECIPITATED AND AGED UNDER DIFFERENT CONDITIONS

By

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It is a well known observation that if a solution of caustic alkali be added to a solution of copper salt, the colour of the precipitated hydroxide changes from blue to black just when a drop of the alkali is added in excess. The colour change is generally assumed to involve the conversion of the blue hydrated copper hydroxide to the black cupric oxide. Evidently, the mechanism of the above conversion brought about by a drop of the alkali does not appear to be easily explainable as a simple dehydration process, involving molecular splitting off of water molecules as shown by the following equation:

$$Cu\,(O\,H)_2.\;x\;H_2O \rightleftharpoons CuO + (x+1)\;H_2O \quad . \quad . \quad . \quad . \quad (1)$$
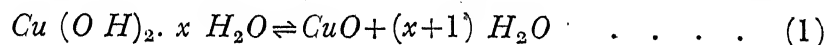
A number of observations recorded below definitely demonstrate that the conversion of hydrated cupric oxide from blue to black variety is not a simple dehydration process. At the same time, it has been shown that the blue precipitate obtained by a deficient amount of the alkali differs in a number of properties from the black precipitate obtained by a slight excess of the alkali. Studies have also been made on the changes exhibited by the hydrated oxide on ageing.

Copper hydroxide was precipitated by the addition of 100.0c. c. of carefully standardised 0.2N caustic soda solution to 50.0c. c. of a 0.2N copper sulphate solution. As the alkali was slowly added to the copper sulphate solution, the colour of the solution went on becoming lighter and lighter, until about half the amount (50c. c.) of
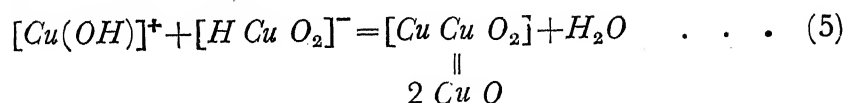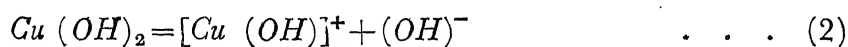
A49-3-4

the alkali had been added, after which the colour began to deepen in shade until deep blue copper hydroxide was precipitated down. The copper hydroxide was filtered off and carefully washed free from sulphate ions. It was observed that althogh just equivalent amount of the alkali had been used, the wash liquor had a little alkaline reaction detectable by the development of pink colour with phenolph-thalein. A similar observation[1] had been made by Tommassi and also by Dey and Ghosh that a solution of sodium chloride and sulphate show an alkaline reaction after shaking with hydrous cupric oxide and it is due to preferential adsorption of the anion. The precipitate was washed free from sulphate ions and was divided into five portions as below:

(1) First portion was placed in 100 c.c. of distilled water.

(2) Second portion was placed in 100 c.c. of N/100 caustic soda solution,

(3) Third portion was placed in 100 c.c. of N/10 caustic soda solution,

(4) Fourth one was dried between filter papers and allowed to remain in air,

(5) Fifth portion was carefully dried by filer papers and placed in a desiccator over concentrated sulphuric acid.

The colour changes of the five portions were observed for about a week. The last one in the desiccator remained definitely deep blue whereas the one in contact with atmosphere remaind bluish though at a number of isolated point it turned brown or grey. The first one in distilled water gradually took up a light grey or brownish shade, the second one became almost definitely black, whereas the third one was deep grey, deeper than the first but lighter than the second. The distilled water in portion (1) was tested after a week and found to be neutral even then.

The above colour changes definitely show that the conve sion of hydrated cupric oxide from blue to black variety is not a simple

dehydration process represented by the equation (1). If the said equation had represented the real process, then the rate of dehydration would have been slower in presence of water than in the dry atmosphere of the desiccator, while as recorded above, actual experimental observations show just the opposite. However, all the above observations can be easily explained by an extension of Kohlschutter and Tuscher's views[2] regarding the blackening of blue copper hydroxide. According to them, the blackening is not due to a molecular splitting off of water, but due to internal neutralisation as a result of amphoteric dissociation of copper hydroxide. Their views can be explained by the following equations:

$$Cu\ (OH)_2 = [Cu\ (OH)]^+ + (OH)^- \qquad \ldots \quad (2)$$

$$Cu\ (OH)_2 = [H\ Cu\ O_2]^- + H^+ \qquad \ldots \quad (3)$$

$$H^+ + (OH)^- = H_2O \qquad \ldots \quad (4)$$

$$[Cu(OH)]^+ + [H\ Cu\ O_2]^- = [Cu\ Cu\ O_2] + H_2O \qquad \ldots \quad (5)$$
$$\underset{2\ Cu\ O}{\parallel}$$

Thus the process is not a simple dehydration process, but involves internal neutralisation of the acidic and basic forms of cupric hydroxide. The blackening cannot occur in the desiccator, where the dissociation into the two forms is not possible, but it can occur in presence of water. The immediate blackening by a drop of the alkali can be easily explained on the above views. Moreover, an extension of the above views can also explain why the blackening, as observed above, is maximum in the presence of $N/100$ alkali and then again is lesser in $N/10$ alkali.

The rate of the process (5) will be proportional to $[(Cu\ OH)^+] \times [(H\ Cu\ O_2)^-]$. It can be easily shown that if $a+b$ is constant, then $a \times b$ has a maximum value when $a = b$. Hence the rate of the above process of blackening shall be the greatest at the point where $[Cu\ (OH)^+] = [(H\ Cu\ O_2)^-]$ or at a pH at which the concentration of the two ions due to acidic and basic dissociation of copper hydroxide are

just equal. The point may be defined as the isoelectric point and can be calculated from the following relationships.

$$\frac{[Cu\,(OH)]^+\,[OH]^-}{[Cu\,(OH)_2]} = Kb \text{ (Basic dissosciation constant).}$$

$$\frac{[H]^+[H\,Cu\,O_2]^-}{[Cu\,(OH)_2]} = Ka \text{ (Acidic dissosciation constant)}$$

Hence $\dfrac{[Cu\,OH]^+[OH]^-}{[H]^+[H\,Cu\,O_2]^-} = \dfrac{Kb}{Ka}$

Now, at the point where $[Cu\,(OH)]^+ = [H\,Cu\,O_2]^-$,

$$\frac{[OH]^-}{[H]^+} = \frac{Kb}{Ka}$$

$$\text{or} \quad \frac{[OH]^{-2}}{Kw} = \frac{Kb}{Ka}$$

$$\therefore [OH]^- = \sqrt{\frac{KbKw}{Ka}}$$

Hence, the blackening will be maximum when the hydroxyl ion concentration is equal to $\sqrt{\dfrac{Kb}{Ka}} \cdot Kw$. As is well known, the basic nature of copper hydroxide represented by Kb is much more pronounced than the acidic nature (represented by Ka). Therefore, the isoelectric point will occur in the alkaline range. Now, if the hydroxyl ion concentration be lesser than this value, the basic form $[Cu\,(OH)]^+$, due to the ionisation shown by the equation (2), will predominate, whereas if the hydroxyl ion concentration be greater than at the isoelectric point, then the acid form $[H\,Cu\,O_2]^-$ arising out of the ionisation shown the equation (3) will be more prominent and hence, in both the cases, the rate of blackening will be slower than that at the isoelectric point. The above discussion explains so simply why the blackening was greatest at a caustic soda concentration of N/100 and was lesser in hydroxyl ion concentration both above and below this value. An effort was made to determine the exact isoelectric point by making acidic buffers of acitic acid sodium acetate mixtures and alkaline buffers of boric acid—borax mixtures. However, it was observed that the borate ions stabilise the blue form due to the ten-

dency of complex formation, hence exact comparisitions could not be made and the exact point could not be determined.

However, the applicability of the theory can be demonstrated by the simple manner in which the observations of a number of previous workers can be easily explained. Tommassi[3] observed that a small concentration of manganous sulphate is able to stabilise the blue colour of copper hydroxide. We have observed that this stabilisation is almost permanent. A sample of the precipitate immersed in a dilute (1 %) solution of manganous sulphate placed on 20th September, 1944 has preserved its original greenish blue shade even after the passage of more than four years. However, we have observed that the stabilisation is not restricted to manganous sulphate, but a number of salts like manganous chloride, zinc suphate, aluminium sulphate and even copper sulphate itself show the phenomenon. A number of conflicting explanations[4,5,6,7,8] have been offered within recent years. Bancroft[4] explains the stabilisation to be due to the protective action of adsorbed hydrous oxide of manganese. On Bancroft's views, Weiser[6] finds it unable to explain the mechanism of stabilisation shown by copper sulphate itself and he supposes the stabilisation to be a phys'cal process depending merely on the size of the particles. Fowles[8] tried to explain the stability to be due to the removal of the adsorbed alkali which by its presence would have catalysed the blackening. Kruger[7] point out that only those substances generally exhibited this stabilisations, which by their hydro:ysis give an acidic solution. Fowle's[8] explanation is very close to ours, which is evident from the discussion given above, that in the acidic medium the blackening will not occur due to the preponderance of the basic form of the copper hydroxide.

Apart from the above variation in the physical characteristics of the copper hydroxide precipitated and aged under different conditions, we have recently observed[9] that the copper hydroxide precipitated with a slight deficient amount of the alkali differs from the one precipitated with a slight excess of the alkali in its dissolubility in dilute ammonia solutions. In this communication, we want to record a

number of qualitative observations made regarding the variation of the properties of the hydroxide precipitated under different conditions and also the variation in the properties of similarly precipitated hydroxide aged under different conditions:

(1) 51.0c. c. of 0.2N caustic soda solution added to 50. 0c. c. of 0. 1M $CuSO_4$ solution

(2) 50. 0c. c. of 0.2N caustic soda solution added to 50. 0c. c. of 0. 1M $CuSO_4$ solution.

(3) 50. 0c. c. of 0.2N caustic soda solution added to 51. 0c. c. of 0. 1M $CuSO_4$ solution.

The precipitates were well washed free from all soluble electrolytes and then allowed to age under the following conditions : precipitates obtained (1), (2) and (3) were each divided into three portions and allowed to stand in contact with the following media:

(a) 100 c. c. of distilled water+2c. c. of 0.2N caustic soda.

(b) 100 c. c. of distilled water,

(c) 100 c. c. of distilled water+2c. c. of 0.2N acetic acid.
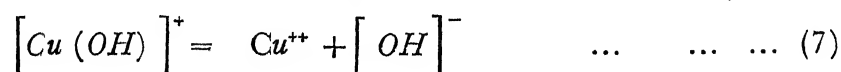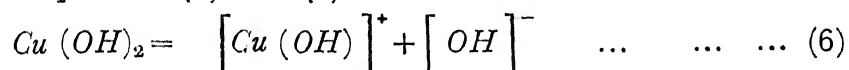
A comparison of the three samples 1 (b), 2(b) and 3(b) aged under distilled water showed that although all the three had become greyish in shade, the first one was almost black, the second one was a little lighter greyish black in shade, while the third one was still lighter in colour. All the samples aged in alkaline solution became almost equally dark grey in a few days time; all the precipitates aged under acidic media retained their blue colour even after six months of ageing.

Now, the solubility of the above samples, after being aged for about ten days, was tested in a solution of Roschelle salt (sodium potassium tartrate) of the same concentration and also in a dilute solution of ammonia. Judged from the colour of the solution, the alkali aged sample (2a) showed much lesser solubility than the acid aged sample (2c) whereas the solubility of the sample (2b) was midway between those of (2a) and (2c) in both sodium potassium tartrate and ammonia solutions. Similarly, a comparison betwen the water aged samp'es (1b), (2b) and (3b) showed similar relationships. The sample (3b) obtained with a slight excess of copper salt showed the maximum solubility,

whereas the sample (1b) showed the minimum solubility of the three samples.

The above variation in the properties and particularly, the similarity in the range of the solubility exhibited in a basic solvent like ammonia and an acidic solvent like sodium potassium tartrate may appear at the first sight a little difficult to explain. However, they can be easily explained by Bronsted's[10], Lowry's[11], or Lewis'[12],[13] views about the nature of acidic and basic substances.

According to Bronsted's and Lowry's conceptions of acid and base, both the ammonia (NH_3) molecule and the tartrate ion are basic in nature, because both of them have a tendency to accept protons. Therefore a similarity in the range of the solubility in the two media can be expected. Moreover, the nature of the dissolving substance being basic, that sort of the precipitate will have the highest tendency to dissolve, which has the portion active in this dissolution in the most acidic form. Cu^{++} and $(CuOH)^+$ ion can be regarded acidic in nature, because they have a tendency to combine with the basic $(OH)^-$ ion, as shown by the equations (6) and (7):

$$Cu\,(OH)_2 = \left[Cu\,(OH)\right]^+ + \left[OH\right]^- \quad \ldots \quad \ldots \quad \ldots \quad (6)$$

$$\left[Cu\,(OH)\right]^+ = Cu^{++} + \left[OH\right]^- \quad \ldots \quad \ldots \quad \ldots \quad (7)$$

Now from the law of mass action, the concentration of these acidic ions, Cu^{++} and $CuOH^+$ will decrease as the concentration of the hydroxyl ions is increased; and therefore with the increasing hydroxyl ion concentration, the solubility in the basic solvents like ammonia and the tartrate ion can be expected to decrease.

According to Lewis' conception, ''the acidic and basic nature of a substance is governed by its tendency to accept or donate electron pairs to form covalent bonds, irrespective of whether the transfer of protons is involved or not''. Now, the solubilty of copper hydroxide in both ammonia as well as the tartrate ions is due to the tendency of copper ions to accept the electron pairs donated by the ammonia molecules

or the tartrate ions with the formation of covalent bonds. Hence, the similarity in the dissolution power of ammonia and the tartrate ions, arising out of the same tendency can be easily understood. Moreover, the above mechanism explains the part played by the surface effects due to the precipitation and ageing of the precipitates under different conditions. The precipitate obtained with an excess of alkali or aged under alkaline solutions will develop a negative charge on the particles due to a preferential adsorption of the hydroxyl ions and this charge will go on decreasing or rather may even change its sign when the precipitation or the ageing is carried out in acidic media. Hence, the particles of the precipitate aged under alkaline media, by virtue of the negative charge on them, will retard the electropositive character of the copper ions to accept electron pairs from either ammonia molecules or the tartrate ions and hence the alkali aged precipitate or the precipitae obtained with a slight excess of the alkali will show a much lesser solubility in ammonia or Roschelle salt than the one aged in acidic media or precipitated with a deficient amount of the alkali.

SUMMARY

1. The rate of blackening of hydrated copper hydroxide has been studied under different conditions.

2. It has been shown that the observations on the rates of blackening can be explained by Kohlschutter and Tuscher's views based on internal neutralisation.

3. The theory of iso-electric point has been developed to explain a greater rate of blackening in the presence of N/100 caustic soda than in the presence of N/10 alkali.

4. The phenomenon of the stabilisation of the blue colour of the hydrated copper hydroxide by manganous sulphate, copper sulphate, zinc sulphate etc. has been explained on the above theory.

5. The variation in the nature of the precipitate obtained and aged under different conditions has been studied.

6. The above variation has been explained by Bronsted's and Lowry's definition of acids and bases and also by G. N. Lewis' "Electronic conception of acids and bases."

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PHYSICO-CHEMICAL STUDIES IN THE FORMATION OF COMPLEX STANNIOXALATES

PART II SPECTROSCOPIC STUDY OF SNCl$_4$-H$_2$C$_2$O$_4$ SYSTEM

By

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(Read on 30th April 1949)

ABSTRACT

Ultra violet absorption spectra of mixtures of stannic chloride and oxalic acid solutions have been studied. From an examination of the photographs of the spectra, it has been concluded that the compounds formed have the compositions: Sn(C$_2$O$_4$)$_2$ and H$_4$Sn(C$_2$O$_4$)$_4$.

In a number of publications we have inferred that stannic tin forms complex compounds with oxalates, malonates and succinates (1, 2) and also with tartrates (3). In the previous part of the present series (4) we have studied the compositions of the complex compounds formed between tetravalent tin and soluble oxalates by the electrical conductivity method. It has already been pointed out by us (5) that since isolation and subsequent chemical analysis fail to convey a true picture of the complex compounds formed, as the products include double salts and adsorption complexes as well, physico-chemical methods must be adopted to elucidate the compositions of complex ions. In persuance to above the absorption spectra of solutions containing the complex stannioxalate ions have now been studied in the ultra violet region and the results interpreted for the determination of the composition of complex ions. This paper records our results on the study of mixtures of stannic chloride and oxalic acid of various compositions.

EXPERIMENTAL

A solution of Schuchardt's stannic chloride crystals was prepared by dissolving an approximately weighed quantity in Merck's dilute

hydrochloric acid solution of known concentration. The solution was carefully estimated by gravimetric method, and diluted and hydrochloric acid added to get a solution of exactly decimolar stannic chloride in normal hydrochloric acid. Hydrochloric acid was needed to prevent hydrolysis. This solution of stannic chloride in hydrochloric acid has been referred to in this paper as stannic chloride solution. Standard solutions of AnalaR oxalic acid were also prepared.

The absorption spectra of individual solutions and also those of the mixtures were photographed as described below. For photographing the spectra Adam Hilger's Constant Deviation Quartz Spectrograph was used with copper are as the source. The photographs were taken on Ilford Empress Plates and an exposure of one minute was allowed in each case. Different thicknesses of the solutions were used for absorption of the radiations by means of a Baly's tube. The experiments were performed at a temperature of 25° C. From the photographs the regions of absorption corresponding to the different thicknesses of the various solutions employed were read. The results are recorded below :

TABLE I

Region of Absorption A.° U.

thickness of solution	Plate 1 M/2 HCl	Plate 2 M/20 SnCl$_4$	Plate 3 M/4 H$_2$C$_2$O$_4$	Plate 4 M/10 SnCl$_4$ + M/2·0 H$_2$C$_2$O$_4$	Plate 5 M/10 SnCl$_4$ + M/2·25 H$_2$C$_2$O$_4$	Plate 6 M/10 SnCl$_4$ + M/2·5 H$_2$C$_2$O$_4$	Plate 7 M/10 SnCl$_4$ + M/3·0 H$_2$C$_2$O$_4$	Plate 8 M/10 SnCl$_4$ + M/3·5 H$_2$C$_2$O$_4$	Plate 9 M/10 SnCl$_4$ + M/4·0 H$_2$C$_2$O$_4$	Plate 10 M/10 SnCl$_4$ + M/5·0 H$_2$C$_2$O$_4$	Plate 11 M/10 SnCl$_4$ + M/8·0 H$_2$C$_2$O$_4$	Plate 12 M/10 SnCl$_4$ + M/10 H$_2$C$_2$O$_4$	Plate 13 M/10 SnCl$_4$ + M/20 H$_2$C$_2$O$_4$	Plate 14 M/10 SnCl$_4$ + M/40 H$_2$C$_2$O$_4$
18mm	2618	2618	3050	3000	3000	2950	2950	2950	2880	2880	2880	2840	2618	2618
16	2618	2618	3050	3000	3000	2950	2950	2880	2880	2880	2840	2840	2618	2618
14	2618	2550	3050	3000	3000	2880	2880	2880	2880	2880	2840	2840	2618	2618
12	2618	2550	3050	3000	3000	2880	2880	2880	2880	2880	2840	2618	2618	2618
10	2550	2550	2890	2880	2880	2880	2880	2880	2880	2800	2618	2618	2618	2618
8	2550	2500	2890	2880	2880	2880	2880	2880	2800	2800	2520	2520	2520	2618
6	2550	2500	2890	2780	2780	2700	2700	2840	2800	2450	2490	2490	2520	2520
4	2550	2460	2770	2780	2780	2700	2700	2618	2450	2450	2450	2490	2470	2480
3	2520	2460	2770	2780	2780	2618	2618	2450	2450	2450	2425	2425	2470	2480
2	2520	2460	2618	2618	2618	2450	2450	2400	2425	2400	2425	2425	2450	2480
1	2520	2425	2425	2618	2350	2350	2350	2350	2350	2350	2350	2425	2325	2400

DISCUSSION OF RESULTS

For the interpretation of the absorption spectra results the shifts in the line 2618 A°.U. were considered. The thicknesses of solutions of different compositions required to produce absorption upto this region are tabulated below.

TABLE II

Ratio $Sn^{iv} : C_2O_4^{--}$	Thickness of solution in mm
1 : 0	18 – 16
1 : 0·25	18 – 8
1 : 0·50	18 – 10
1 : 1·00	12 – 10
1 : 1·25	10
1 : 2·00	5·4
1 : 2·50	5·4
1 : 2·86	4
1 : 3·33	3
1 : 4·00	3
1 : 4·44	2
1 : 5·00	2
1 : ∝	2

A graph was then plotted showing the change in the required thicknesses with change in compositions of the mixture. A perusal of the curve shows that the first break in the curve occurs at the point corresponding to 2 of oxalate for 1 of tin, and this point may, therefore, be assigned to the formation of normal stannic oxalate. As the formation of stannic oxalate is complete, complex formation seems to commence and the formation of the complex is finally complete at 4 of oxalate for 1 of tin, where there is the last break in the curve and then the curve smoothly parallel to the axis. Thus we conclude that the absorption spectra also leads us to the inference of the formation of $Sn(C_2O_4)_2$ and $H_4Sn(C_2O_4)_4$ in a mixture of solutions of stannic chloride and oxalic acid, which

is in agreement with the results arrived at by the electrical conductivity of stannic hydroxide-soluble oxalate system, as reported in a previous part of the series.

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INSTRUCTIONS TO CONTRIBUTORS

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